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(57) Abstract

The present invention provides an ion conducting matrix comprising: (i) 5 to 60 % by volume of an inorganic powder having a good aqueous electrolyte absorption capacity; (ii) 5 to 50 % by volume of a polymeric binder that is chemically compatible with an aqueous electrolyte; and (iii) 10 to 90 % by volume of an aqueous electrolyte, wherein the inorganic powder comprises essentially sub-micron particles. The present invention further provides a membrane being a film made of the matrix of the invention and a composite electrode comprising 10 to 70 % by volume of the matrix of the invention.

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ION CONDUCTIVE MATRIXES AND THEIR USE

FIELD OF THE INVENTION

The present invention relates to ion conductive matrixes, membranes and electrodes, their manufacture and use. In particular, the present invention is concerned with membranes comprising composite polymeric films and
5 composite polymers.

BACKGROUND OF THE INVENTION

Ion conducting membranes (to be referred to hereinafter as "ICM") are to be found in many electrochemical cells, among which: fuel cells, electrolyzers, electrochromic cells, batteries, electrochemical sensors and
10 others. In some cases, polymer electrolyte is used such as Nafion. However, Nafion based fuel cells suffer from two major disadvantages. The first is that Nafion is a very expensive material and the second, its characteristic to dry out during the fuel cell operation due to water dragging by the protons conducted.

15 US 5,456,600 teaches the use of a polymeric membrane for making an lithium-ion rechargeable battery cell. The membrane disclosed is a combination of a poly(vinylidene fluoride) copolymer matrix and a compatible organic solvent plasticizer which maintains a homogenous composition in the form of a flexible, self-supporting film.

US 5,643,689 discloses a non-liquid proton conductor membrane which comprises a matrix polymer dissolvable in a solvent and an acidic multimer dissolvable in that solvent. In accordance with the disclosure of this publication, when the membrane is contacted with a second solvent, it swells
5 to allow an improved electrical contact between the cathode and anode plates in which the membrane is interposed.

Another type of polymer membrane is described in US 5,425,865. The membranes described comprise a porous matrix of a crosslinked polymeric material, and a second polymeric material that partially
10 blocks the pores of that matrix.

Another type of cell is the phosphoric acid fuel cell (PAFC), wherein acid is absorbed in a porous matrix made of e.g. silicon carbide powder and metal phosphate or metal oxide or metal salt. Typically, such a cell operates at elevated temperatures, about 180⁰ to 200⁰C. US 4,623,415 describes a
15 membrane comprising a porous matrix for retaining phosphoric acid electrolyte where the matrix consists of a substance which is unreactive with phosphoric acid and has electron insulating properties.

SUMMARY OF THE INVENTION

20 It is an object of the present invention to provide a novel, low cost and highly conductive ion conducting matrix, i.e. a matrix in which ions derived from acids, bases or salts are mobile.

It is another object of the present invention to provide novel, low cost and highly conductive ion conducting membranes and electrodes.

25 Another object of the present invention is to provide electrochemical cells comprising the matrixes of the invention.

It is yet a further object of the invention to provide methods for preparing such membranes and electrodes.

Still, it is the object of the present invention to provide uses for the ion conducting membranes and electrodes of the invention.

Other objects of the invention will become apparent as the description of the invention proceeds.

5 Thus, the present invention provides by the first of its aspects an ion conducting matrix comprising:

- (i) 5% to 60% by volume of an inorganic powder having a good aqueous electrolyte absorption capacity;
- (ii) 5% to 50% by volume of a polymeric binder that is chemically
10 compatible with an aqueous electrolyte; and
- (iii) 10 to 90% by volume of an aqueous electrolyte,

wherein the inorganic powder comprises essentially sub-micron particles, preferably from about 5 to about 150 nm in size. The matrix of the present invention may optionally comprise between about 0.1% to about 25% of a
15 non-volatile liquid lubricant that is chemically compatible with all the components in the matrix.

In accordance with a preferred embodiment of the present invention, the inorganic powder is characterized in that it has a surface area of at least 10 m²/g, and possesses a good absorption capability for the aqueous electrolyte.

20 According to another aspect of the invention, there is provided a membrane being a film made of the matrix of the invention.

According to a further aspect of the invention, there is provided a composite electrode comprising 10 to 70% by volume of the matrix of the invention and the balance is made essentially by an electrode material, which
25 is a material known in the art *per se* as a suitable material in the manufacturing of electrodes, eg. carbon, graphite, air, oxygen, H₂, methanol electrodes, Zn, Cd, Ni, Pb, Fe, Cu or their alloys, **metal oxide electrodes, e.g.** RuO₂, WO_x, MnO₂, NiOOH, AgO, Ag₂O and the like.

In the case that the matrix of the invention is used as an ion conducting matrix in a composite electrode, the inorganic powder may be electronically conductive.

Preferably, the inorganic powder of the matrix of the present invention is a member selected from the group consisting of SiO_2 , ZrO_2 , B_2O_3 , TiO_2 , Al_2O_3 and the like.

The polymeric binder used in the matrix of the present invention is a material which is chemically compatible with an aqueous electrolyte used, i.e. non-soluble in that electrolyte, and is a member selected from the group consisting of: polyvinylidene fluoride (PVDF), PVDF-hexafluoropropylene (PVDHFP), poly(tetrafluoroethylene) (PTFE), poly(methylmethacrylate) (PMMA), polysulfone amide, poly(acrylamide), polyvinyl chloride (PVC), poly(acrylonitrile), polyvinyl fluoride and any combination thereof.

The aqueous electrolyte of the present invention consists of an aqueous soluble compound selected from a salt, a base or mixtures thereof. Examples of aqueous soluble salts are alkali metal salts, alkali earth metal salts, R_4NX where R is hydrogen or an organic radical and X is an anion derived from an inorganic acid, NH_4Cl , ZnCl_2 and any combinations thereof.

Examples of aqueous soluble bases for use in the present invention are R_4NOH where R is hydrogen or an organic radical, alkali or alkali earth base compounds and any combinations thereof.

In the case that the matrix of the invention is used as a proton conducting matrix, it is referred to hereinafter as "PCM". The acid according to the present invention, which may be also a mixture of acids, may be a pure acid or an acid dissolved in water or in another suitable non-aqueous solvent that is known *per se* in the art. Acids suitable according to the present invention are: $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$, $\text{HO}_3\text{S}(\text{CF}_2)_n\text{SO}_3\text{H}$ wherein n is an integer having a value of 0 to 9, sulfuric acid, HCl , HBr , phosphoric acid, HNO_3 and the like. Preferred acids are $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$ or $\text{HO}_3\text{S}(\text{CF}_2)_n\text{SO}_3\text{H}$ where n is

equal to 0,1,2,3 or 4. These preferred acids can be used either in their pure form or as aqueous solutions having a molar concentration of 10 to 99%, and preferably a molar concentration of 25% to 99%.

The ICM of the present invention has the general appearance of a plastic film, having good mechanical properties. It can typically be bent to about 180° with no substantial fractures occurring, and it can be prepared in thickness being in the range of from about 10 to about 1000 microns or more. Due to its stability and good ionic conductivity, it can be used at a large temperature range of from sub-zero to about 150°C.

According to a preferred embodiment of the invention, where the matrix is in the preparation of a membrane, the inorganic powder comprised in the matrix is a very fine, electronically non-conductive powder having a particle size of preferably less than 150 nm. According to this embodiment, the ICM pores in which the aqueous electrolyte is absorbed are very small, and their characteristic dimension is essentially smaller than 50 nm.

The absorption capacity or the retention capability of the membrane for the acid or the aqueous electrolyte used depends on several parameters, among which are the composition and the type of the inorganic powder, the polymeric binder and the type of the dissolved acid or electrolyte. The combination of these parameters should be optimized in order to tailor the product for each application. While carrying out such optimization, consideration should be given to the fact that the highest the content of inorganic powder is, the inferior the mechanical properties become. Increasing the inorganic powder content of the matrix increases its electrolyte retention characteristic, but at the same time, decreases its mechanical strength. On the other hand, increasing the polymeric binder in the matrix increases the strength of the latter, but decreases the wettability of the matrix thus turning it to a less conductive one.

According to yet another embodiment of the invention, an improvement of the matrix wettability and consequently the electrolyte retention, is achieved by adding to the membrane multi valance metal salts such as Al, Zr, B, Ti and the like.

- 5 According to another embodiment of the invention, the improvement of the matrix wettability and consequently the electrolyte retention is achieved by pre-treating the inorganic powder with an acid or a base prior to the preparation of the membrane.

The elasticity and elongation of ICMs that are rich in inorganic powder
10 and that of electrodes based on these materials were improved by the addition of low to medium molecular weight (typically 100 to 7500 mass units) oil or oil like liquid materials that serve as an internal lubricant between the molecules of the polymer binder. The main effects of the internal lubricant are to increase the distance between the polymer chains, thus reducing the
15 attraction forces between the polymer molecules and/or replacing the original attraction forces between the polymer molecules with lower attraction forces between the internal lubricant molecules and/or becoming a separation layer between the polymer molecules. ICMs that contain an internal lubricant have smaller resistance to external forces because the polymer chains can slide
20 more easily one over the other. It is essential that these materials have low vapor pressure and are compatible with all other components at the relevant temperatures of application. In order to reduce the escape effects of an internal lubricant from the ICM (lower migration rates of these materials to the surface of the polymer) it is recommended, according to the present
25 invention, to use an internal lubricant with a low vapor pressure, to use liquid polymeric internal lubricants or to chemically link the internal lubricant to the polymer molecules. Some of these lubricants may be useful only at room temperature and at mild conditions (e.g. not in strong acids or bases).

It was found, according to the present invention, that during the preparation process one of the following factors must be controlled:

- a) The solubility parameter (δ - factor) of the internal lubricant should not differ by more than $5 \text{ (cal/cc)}^{1/2}$ units from that of the polymer.
- 5 b) The solubility parameter (δ - factor) of the mixture of an internal lubricant or lubricants (in case of a combination of lubricants) and the solvent or solvents (in case of a mixture of solvents) will not differ by more than 5 units from that of the polymer of the matrix.

(Solubility parameters are defined in: "Polymer Handbook",
10 Interscience Publishers, a division of John Wiley & Sons, 1966, pp. IV-344 - IV-367; J.E. Mark, Physical Properties of Polymers Handbook, American Institute of Physics, Woodbury, New York, 1996. pp. 231-237 and R.C. Weast, CRC Hand Book of Chemistry and Physics, 56th Edition, 1975-1976, published by CRC Press.)

15

There is an advantage in using internal lubricants that have a low solubility in water so as to achieve a solubility factor which is not higher than $14 \text{ (cal/cc)}^{1/2}$, preferably not higher than $10 \text{ (cal/cc)}^{1/2}$. The low solubility prevents the migration of internal lubricant out of the ICMs when they come
20 in contact with water at the washing phase or at the acid loading phase.

The internal liquid lubricant materials are selected, for example, from the following materials: diesters of aliphatic and aromatic dibasic acids such as, for example, adipic acid, phthalic acid and sebacic acid, esters of phosphoric acid, hydrocarbons and synthetic hydrocarbons such as decan,
25 dodecan, etc., machine oil, silicone oils, fluorocarbons such as perfluoropolyethers, for example: $\text{CF}_3\text{O}[-\text{CF}(\text{CF}_3)-\text{CF}_2\text{O}]_x(-\text{CF}_2\text{O})_y\text{CF}_3$, x being between 0 and 50 and y between 0 and 100. It was found that the addition of these lubricants increases in some cases the conductivity of the ICM by over 30%.

Still by another embodiment of the present invention, there is provided a membrane as described above that is mechanically reinforced. The reinforcement can be done by any way known *per se* in the art, e.g., including in the membrane an electronically non-conductive screen, felt, fibers or any other reinforcing element as known in the art.

The ion conducting membranes of the invention may be prepared by any one of several methods, which are also encompassed by the present invention, among which are casting and extrusion. The method for casting an ICM according to the present invention comprises the following steps:

10

- (i) preparing a mixture comprising an inorganic powder, a polymeric binder that is chemically compatible with an aqueous electrolyte, at least one solvent characterized in having a high boiling point of above 100⁰C and at least one low boiling point solvent, having a boiling point lower than that of the high boiling point solvent(s), in which the polymeric binder is soluble or form a gel at the casting temperature;
- (ii) casting a film out of the mixture;
- (iii) allowing the low boiling point solvent to evaporate from the mixture, thus forming a solid film;
- (iv) washing the solid film and replacing the high boiling point solvent with the desired aqueous electrolyte solution to be included in the membrane.

25

According to a preferred embodiment of the invention, the mixture is prepared in a paste-like gel or gel form and is introduced into a mold to obtain the required film form. The evaporation of the low boiling solvent as described in step (iii) should not necessarily be completed prior to proceeding

to step (iv), and it may suffice that a solid film which can be further processed, is obtained. The film is then washed, preferably first with water and then with the electrolyte to be absorbed in the matrix, forming the required membrane. This step is carried preferably at a temperature of less
5 than 150°C. The use of water or the electrolyte may be done by repeating immersions of the film therein so as to displace the water or the high boiling solvent, as applicable. Preferably, the last immersion is conducted at an elevated temperature so as to evaporate the solvent and allow the aqueous electrolyte solution to replace it in the membrane formed. When using a water
10 non-soluble high boiling point solvent, the process involves washing the solid film with another solvent that is water soluble, followed by washing the solid film with water.

When casting a composite electrode which comprises the matrix of the present invention, the mixture prepared in step (i) of the above-described
15 method, comprises a further powder of the suitable electrode material. The remaining steps of the process are carried *mutatis mutandis* as described in the method for casting an ICM.

According to a further embodiment of the invention, the high boiling point solvent is a water soluble solvent, and is preferably a member selected
20 from the group consisting of propylene carbonate (PC), ethylene carbonate (EC), dimethyl phthalate, diethyl phthalate, dibutyl phthalate and the like of any combinations thereof.

According to another embodiment of the invention, the low boiling point solvent is a member selected from the group consisting of
25 tetrahydrofuran (THF), DME, cyclopentanone, acetone, N-methyl pyrrolidone (NMP), dimethylacetamide (DMAC), methylethylketone (MEK), dimethylformamide and the like, or any combination thereof.

The method for extruding an ICM according to the invention comprises the following steps:

- 5 (i) preparing a mixture comprising an inorganic powder, a polymeric binder that is chemically compatible with an aqueous electrolyte and at least one solvent characterized in having a boiling point of above 90°C in which the polymeric binder is at least partially soluble or form a gel at extrusion temperature;
- (ii) heating the mixture to its softening temperature;
- (iii) forming a film out of the mixture by hot extruding the softened mixture;
- 10 (iv) cooling the film thus formed;
- (v) washing the solid film and replacing the solvent with the desired aqueous electrolyte solution to be included in the membrane.

15 When extruding a composite electrode which comprises the matrix of the present invention, the mixture prepared in step (i) of the above-described method comprises a further powder of the suitable electrode material. The remaining steps of the process are carried *mutatis mutandis* as described in the method of extruding an ICM.

20 According to a preferred embodiment of the invention, the solvent suitable for the extrusion method is a water soluble solvent being a member selected from the group consisting of propylene carbonate, diethyl carbonate, dimethyl carbonate, butyrolactone, methyl isoamyl ketone, cyclohexanone, dialkyl phthalate, glycerol triacetate and the like or any combinations thereof.

25 The washing of the film described in step (v) is preferably done first with water and then with the aqueous electrolyte to be dissolved into the matrix, to form the required membrane. Water or the electrolyte is applied by repeatedly immersing the film therein so as to displace the water or the solvent, as applicable.

Another aspect of the invention concerns possible uses of the matrixes of the invention. One such use is the manufacture of electrochemical cells that are substantially free from mobile liquid electrolyte solution. Electrochemical cells may comprise an ICM sandwiched by two electrodes. Such electrodes
5 are carbon or graphite, Zn, Fe, Cd, Ni, Cu, Al and their alloys; electrodes or metal oxide electrodes, e.g. of RuO_2 , WO_x , MnO_2 , NiOOH , AgO , Ag_2O and the like. This type of a cell may be manufactured by using a hot press technique. In this process, the two electrodes and the ICM therebetween are pressed together at the softening temperature of the binder, with or without a
10 solvent, typically at a temperature in the range of from about 60° to 150° and under 20 to 1000 Kg/cm^2 for about 1 to 10 minutes, obtaining a single structural cell unit with improved mechanical strength and performance.

According to a preferred embodiment of the invention, a Zn cell may also be manufactured by hot pressing together a cathode, an anode and an
15 ICM therebetween. In this process the anode consists of a ceramic powder binder such as PVDF and Zn in the form of a fine powder; the cathode may also consist of PVDF, ceramic powder, a metal oxide such as MnO_2 and a small amount of carbon or graphite. In case that a Zn air cell is assembled, the cathode is a commercial air electrode made of platinum or another
20 catalyst supported on carbon or graphite particles, paper or felt.

Cells such as Zn/air or Zn/oxygen cells consist of: 1) a composite Zn electrode made typically of about 30% v/v the ICM matrix and 70% of Zn in the form of a fine powder. The preferred Zn powder consists of up to 0.1% (w/w) Hg, Sn, In, Bi, Pb or mixture thereof for corrosion prevention; 2) an
25 ICM; 3) an oxygen or air electrode. The air or oxygen electrode consists of a catalyst selected from Pt, Pd, W, Mn, Cu, Ag, Ni or their mixture or their oxides supported by carbon or graphite powder. The amount of the catalyst is from about 5% to about 50% w/w relative to the carbon or graphite powder.

One side of the air or oxygen electrode is hydrophilic and the other side is hydrophobic. Commercially available air or oxygen electrodes can be used or they can be made with the ICM matrix where the hydrophobic side contains more than 25% v/v polymer, preferably Teflon and no ceramic powder.

For example, according to the present invention, nickel-cadmium and nickel-iron batteries consist of a cathode made of NiOOH powder and the ICM matrix, while the anode is made of either cadmium based powder and ICM matrix or iron based powder and the ICM matrix.

In all cases, the polymer binder must be chemically compatible with both the electrolyte and the electrode materials. For alkali solutions, binders such as Teflon (PTFE), polycarbonate, PVC, polypropylene and rubber are preferred.

Other uses according to the present invention include lead acid battery where one or both electrodes are composite electrodes which comprise the proton conducting matrix of the invention. Also, the present invention encompasses lead acid batteries comprising PCMs of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS:

Fig. 1 presents results of conductivity measurements for PCMs prepared in accordance with the present invention; and

Fig.2 illustrates the charge-discharge cycles of a capacitor disclosed in Example 10.

The following examples are not to be construed as limiting the invention as described herein.

EXAMPLES

Example 1

A membrane film was manufactured by mixing 0.170 g of powdered
 5 Kynar PVDF 2801-00 and 0.147 gr of high surface area, amorphous fumes
 particle size $400 \text{ m}^2/\text{g}$ silicon (IV) oxide, 99.8% Alfa Aesar by A. Johnson
 Matthey Company, with a 20 ml. of cyclopentanone and 0.48 ml of propylene
 carbonate (PC). The viscous mixture obtained, was poured onto a Teflon plate
 and was allowed to dry at room temperature for 24 hours. Thereafter, a
 10 flexible, strong, transparent film was obtained.

The film was washed by using double distilled water in order to
 remove the PC. Following the washing, the film became less transparent, but
 possessed higher mechanical strength. In the Tables presented in the
 proceeding Examples, the following terms are used to describe mechanical
 15 properties: Bad – denotes a membrane which can easily be torn by hand,
 Good - denotes a membrane that is not easily torn by hand,
 Very Good denotes a membrane for which rupture extensive force is required.

In the same manner, other samples were made in different
 compositions as can be seen in Table 1.

20 **TABLE 1:** ICM composition and mechanical properties

Sample No.	SiO ₂ vol. %	PVDF vol. %	Porosity vol. %	ICM mechanical properties
1	0.5	24.5	75%	Very Good
2	0.5	24.5	75%	Very Good
3	1.0	24.0	75%	Very Good
4	2.8	37.2	60%	----
5	2.5	22.5	75%	Very Good

6	3.5	21.5	75%	Good
7	5.0	37.2	75%	-----
8	9.6	22.4	68%	Bad
9	10.0	15.0	75%	Very Good
10	12.8	19.2	68%	Bad
11	8.0	12.0	80%	Very Good
12	12.5	12.5	75%	Bad
13	5.0	5.0	90%	Bad
14	15.0	10.0	75%	Bad

Samples number 9 and 11 exhibited the best wetting and capillary properties. This sample after water wash could be bent 180% without causing any damage to the film. Moreover, an acid wet film was heated at 110⁰ C for several hours, and its structure remained intact and its capillary properties did not change. The pore size distribution of this ICM was measured using Quantachrome NOVA 2200 Surface Area Analyzer. It was found that a significant volume (above 15%) of the nanosize pores had a diameter smaller than 3 nm.

The thickness of the ICMs described in Table 1 were in the range of 0.05 to 1mm.

Example 2

A membrane film was manufactured by mixing 0.850 gr of powdered Kynar PVDF 2801-00 with 1.363 gr of high surface area Titania, in 25 ml cyclopentanone with 2.4 ml of PC. The viscous mixture was poured on a Teflon plate as described in Example 1 and was allowed to dry at room temperature for 24 hours. Thereafter, a flexible, opaque white film with very good mechanical strength was obtained.

The film was washed with double distilled water, similarly to the treatment in Example 1. In the same manner, other samples were prepared while different compositions were used. The results obtained are given in Table 2.

5

TABLE 2: ICM composition and mechanical properties

Sample No.	TiO ₂ vol. %	PVDF vol. %	Porosity vol. %	ICM mechanical properties
1	2.5	22.5	75%	Very Good
2	7.5	17.5	75%	Very Good
3	10.0	15.0	75%	Very Good

Example 3

A membrane film was manufactured by mixing 0.85 gr of Kynar PVDF 2801-00 with 1.270 gr of micropolish 0.05 micron gamma Alumina manufactured by Buehler, in 20 ml of acetone with 2.4 ml of PC. The viscous mixture was poured on a Teflon plate as described in the preceding examples. A flexible, opaque white film having very good mechanical strength was thus obtained.

Example 4

A film prepared according to the description given for sample No. 9 of Example 1 was immersed in several aqueous solutions of trifluoromethane sulfuric acid (TFMSA) in acid to water v/v ratios of 1:1, 1:15, 1:2 and 1:3 for 3 hours under room conditions. The conductivity of the PCMs thus obtained was measured by using AC impedance spectroscopy Solartron model SF 1260. The measurements were made while using two

1 cm² stainless steel electrodes. The results presented in Fig. 1 indicate that the conductivity was practically the same for all PCMs where acid to water v/v ratio was in the range of 1:1 to 1:3, with a slightly higher conductivity, of 0.132 S/cm at 25⁰C, for the PCM comprising the 1:2 acid to water v/v
5 content.

Example 5

A film of sample No. 9 (Table 1) was immersed in ether and a 0.1M or 1M KOH for periods of 1 min. or 1 hr., and then immersed in different volume concentration solutions of TFMSA as described in Example 4 to
10 form PCM. The PCMs conductivity was measured as described in Example 4. The results obtained indicated that the wetting properties of the base treated PCMs were improved while its conductivity was not significantly changed.

Example 6

15 A PCM was formed by immersing the film of sample No. 9 (Table 1) in a 1:2 TFMSA to water solution (v/v) for 2.5 hours at 90⁰C. The conductivity of the PCM was measured as described in Example 4, and an increase of about 20% was found in its conductivity at room temperature over a PCM which was acid treated at such temperature.

20 Example 7

A PCM film was formed by immersing films of samples No. 11 and 13 (Table 1) in a 1:2 acid to water solution (v/v) for 3.5 hrs. at room temperature. The conductivity was measured as was described in Example

4. The conductivity found was 0.108 and 0.126 S/cm for samples No. 11 and 13, respectively.

Example 8

A PCM was formed by immersing films of samples No. 11 and 13 (Table 1) in aqueous solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ 1:3 v/v or in concentrated H_2SO_4 for 3.5 hrs. at room temperature. The conductivity of the PCM thus obtained was measured as was described in Example 4. The results measured for sample No. 11 were about 0.038 and about 0.179 S/cm for concentrated H_2SO_4 and 1:3 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$, respectively, whereas the results measured for sample No. 13 were about 0.058 and about 0.207 S/cm for concentrated H_2SO_4 and 1:3 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ respectively.

Example 9

A film of sample No. 9 (Table 1) was immersed in aqueous solution of $\text{CF}_3\text{SO}_3\text{H}:\text{H}_2\text{O}$ 1:3 (v/v) for 2.5 hrs. The PCM thus obtained was hot pressed with a carbon electrode which comprised 40% (v/v) of the combination. The heating of the two films was carried out between two polished stainless steel pellets sprayed with decan, in order to prevent sticking to the stainless steel pellets. The process was conducted at 130°C and under 7 atm, for the period of 15 sec. The PCM and carbon electrode adhered to each other in a good form.

Example 10

A double layer capacitor having two Ti foils as current collectors, was assembled. Two 4.91cm^2 composite carbon electrodes were mounted

on both sides of a PCM prepared in accordance with the disclosure of Example 6. Each carbon electrode was comprised of two layers: the first layer was a 0.3 mm thick porous layer, made of 15% SiO₂, 5% oxidized Shawinigm Blac, 50% oxidized Graphite, 10% Teflon and 10% Graphite fibers, pressed under 100 kg/cm². The second layer was a 1 mm impermeable layer made of 65% Graphite, 15% Teflon and 20% Graphite fibers, pressed under 1000 kg/cm². Before assembling the cell, the carbon electrodes were sprayed with the 1:2 TFMSA: water solution. The capacitor was charged and discharged under a current of 20 mA, using Maccor 2000 Tester with voltage of 0.01 to 1.2V. The graph illustrating the charge and discharge is presented in Fig. 2.

Example 11

A membrane film was manufactured by mixing 0.85 gr of Kynar PVDF 2801-00 with 0.682 gr of Degussa Titandioxid P25, 0.368 gr of Johnson Matthey Silicon (IV) Oxide, 15 ml cyclopentanone and 2.4 ml of PC. The viscous mixture was poured on a Teflon plate as described in the preceding examples. A flexible, opaque white film having very good mechanical strength was thus obtained.

Example 12

Samples prepared as described in Examples 2,3 and 11, were immersed in aqueous solution of 1:2 of TFMSA:H₂O (v/v) for 1 to 1.5 hours at approximately 100°C. The conductivity of the PCMs was measured as described in the preceding examples. The results were the following: the PCM conductivity of sample 2 (Table 2) was 0.032 S/cm; the conductivity

of Example 3 PCM – 0.020 S/cm, and the conductivity of Example 11 PCM - 0.04 S/cm.

Example 13

The pore size distribution of the PCM described in sample 9 of Table 1 was measured by using Quantachrome NOVA 2200 Surface Area Analyzer. It was found that a significant volume of the material tested had nanosize pores having a characteristic dimension of less than 8 nm. These nanosize pores have good retention capability for the acid and are small enough to prevent gas bubbles to cross over the PCM. This property is of importance in the case where the PCM of the invention is used for fuel cell applications.

Example 14

A film prepared according to the description given for sample No. 9 in Example 1 was immersed in several aqueous solutions of KOH. The results are summarized in Table 3.

TABLE 3 – Characterization of KOH Based ICM

ICM	KOH Concentration [M]	Resistance [Ω]	Thickness [μm]	σ [S/cm]
1	1	0.0869	65	0.0747
2	1	0.0808	65	0.0804
3	1	0.0862	65	0.0754
3	1	0.2140	175	0.0817
4	2	0.0473	65	0.1374
5	2	0.0467	75	0.1605
6	2	0.0486	70	0.1440
7	2	0.1372	155	0.1129

Example 15

A double layer capacitor having two Ti foils as current collectors, was assembled. Two 4.91cm^2 composite carbon electrodes, were mounted on both sides of an ICM prepared in accordance with the disclosure of Example 5. Each carbon electrode was comprised of two layers: the first layer was a 0.3 mm thick porous layer, made of 15% SiO_2 , 5% oxidized Shawinigm Blac, 50% oxidized Graphite, 10% Teflon and 10% Graphite fibers, pressed under 100 kg/cm^2 . The second layer was a 1 mm impermeable layer made of 65% Graphite, 15% Teflon and 20% Graphite fibers, pressed under 1000 kg/cm^2 . Before assembling the cell, the carbon electrodes were sprayed with the 1M KOH solution. The capacitor was charged and discharged under a current of 10 mA, using Maccor 2000 Tester with voltage of 0.01 to 1.0V, and had a capacitance of 0.1F.

Example 16

An ion conducting membrane (ICM) was made by immersing the film of sample No. 9 (Table 1) in a 2M NH_4Cl aqueous solution. The conductivity was measured at room temperature by using AC impedance spectroscopy Solartron model SF 1260. The measurements were made while using two 1 cm^2 stainless steel electrodes. The conductivity was 0.04 S/cm.

Example 17

A cell having two Ti foils as current collectors was assembled. The 100 microns thick anode was 60% porous and the solid matrix consisted of 35% (v:v) PVDF and 65% fine Zn powder which contains 0.1% Hg. The 100 microns thick cathode was 60% porous and its solid matrix consisted of

35% (v:v) PVDF, 5% fine powder graphite and 60% fine powder MnO_2 . A 100 microns thick ICM prepared in Example 16 was hot pressed between 1 cm^2 cathode and 1 cm^2 anode. The whole cell was immersed in 2M NH_4Cl aqueous solution in order to fill all the pores. The excess of electrolyte was
5 cleaned and the cell was held between the two Ti current collectors. The cell was discharged at 0.1 mA for 15 hours to 0.7V end voltage.

Example 18

A Zn air cell was assembled according to Example 17, except the electrolyte was 1M KOH. The cathode used was a commercial air electrode
10 purchased from Electrochem. The cell was discharged at 0.1 mA for 25 hours and at an average voltage of 1.2V.

Example 19

A membrane film was manufactured by mixing 1.53 g. of powdered Kynar PVDF 2801-00 and 1.84 gr of high surface area,
15 16 nm particle size silicon dioxide, > 99.8% (Degussa), 0.3 ml of Silicon oil (Wacker Chemie 500 AP), with a 43 ml. of cyclopentanone and 8 ml. of propylene carbonate (PC). The viscous mixture obtained, was poured onto K control coater (R K Print, Coat Instruments) and a film was made by using the doctor blade method. The film was allowed to dry at room temperature for a
20 couple of hours. An elastic strong transparent film was obtained.

The film was washed with double distilled water in order to remove the PC, and it was immersed in 30% wt H_2SO_4 for 1.5 hours at 100°C . The conductivity of the PCM thus obtained was measured by using AC impedance spectroscopy Solartron model SF 1260. The measurements were conducted
25 while using two 1 cm^2 Ti electrodes.

Example 20

In the same manner, other PCM samples were prepared with different compositions. Their qualitative elongation and conductivity have been determined (Table 4).

5

TABLE 4: PCM Composition, Conductivity and Elongation

Sample No.	PVDF Vol. %	Internal lubricant	Vol. % of internal lubricant	Conductivity [S/cm]	Elongation
1	9	Decane	3	0.44	Good
2	9	Yivac 06/6	3	0.34	Good
3	10	Paraffin	2	0.38	Good
4	6	Silicon Oil	6	0.38	Bad
5	6	Synthetic oil	6	0.44	Medium
6	6	Decane	6	0.47	Medium
7	6	Yivac 06/6	6	0.37	Medium

All PCM's contain 8% v/v silica, and they are about 80% porous.

Yivac 06/6 is a perfluoropolyether of the general formula

10 $\text{CF}_3\text{O}[-\text{CF}(\text{CF}_3)\text{CF}_2\text{O}-]_x(-\text{CF}_2\text{O}-)_y\text{CF}_3$, M.W. 1800, purchased from Edwards.

The thickness of the PCM's described in Table 4 was in the range of 0.08 to 0.1mm.

CLAIMS:

1. An ion conducting matrix comprising:
 - 5 (i) 5% to 60% by volume of an inorganic powder having a good aqueous electrolyte absorption capacity;
 - (ii) 5% to 50% by volume of a polymeric binder that is chemically compatible with an aqueous electrolyte; and
 - (iii) 10 to 90% by volume of an aqueous electrolyte,
- 10 wherein the inorganic powder comprises essentially sub-micron particles.
2. A matrix according to claim 1 that is a proton conducting matrix, comprising
 - 15 (i) 5% to 50% of an inorganic powder having a good acid absorption capacity;
 - (ii) 5% to 50% by volume of acid chemically compatible polymeric binder; and
 - (iii) 10 to 90% by volume of an acid,
- 20 wherein the inorganic powder comprises essentially sub-micron particles.
3. A matrix according to claim 1 or 2, optionally comprising between about 0.1% to about 25% by volume of a non-volatile liquid lubricant material that is chemically compatible with all the components in the
- 25 matrix.

4. A matrix according to claim 3, wherein said lubricant is a member selected from the group consisting of diesters of aliphatic and aromatic dibasic acids, esters of phosphoric acid, hydrocarbons and synthetic
5 hydrocarbons, silicone oils, fluorocarbons and mixtures thereof.

5. A matrix according to any one of the preceding claims, wherein said inorganic powder is a powder having a surface area of at least $10 \text{ m}^2/\text{g}$ and possesses a good absorption capability for said aqueous electrolyte.

6. A matrix according to claim 5, wherein said inorganic powder is a
10 member selected from the group consisting of SiO_2 , ZrO_2 , B_2O_3 , TiO_2 , Al_2O_3 and optionally hydroxides and oxy-hydroxy of Ti, Al, B and Zr, and any combination thereof.

7. A matrix according to any one of the preceding claims, wherein said polymeric binder is a material which is a member selected from the group
15 consisting of: polyvinyliden fluoride, polyvinyliden fluoridehexafluoropropylene, poly(tetrafluoroethylene), poly(methylmethacrylate), polysulfone amide, poly(acrylamide), polyvinyl chloride, poly(acrylonitrile), polyvinyl fluoride and any combination thereof.

8. A matrix according to any one of the preceding claims, wherein said
20 aqueous electrolyte consists of an aqueous soluble compound selected from a salt, a base or mixtures thereof.

9. A matrix according to claim 8, wherein said aqueous soluble salt is a member selected from the group consisting of alkali metal salts, alkali earth metal salts, R_4NX , where R is an organic radical and X is an anion derived
25 from an inorganic acid, NH_4Cl , ZnCl_2 and any combinations thereof.

10. A matrix according to claim 8, wherein said aqueous soluble base is a member selected from the group consisting of R_4NOH where R is hydrogen or an organic radical, alkali or alkali earth base compounds and any combinations thereof.

11. A matrix according to claim 1 or 3, wherein said aqueous electrolyte is used in an aqueous solution having a molar concentration of from about 0.1M to about 10M.
12. A matrix according to claim 11, wherein the aqueous electrolyte has a
5 molar concentration of from about 1M to about 5M.
13. A matrix according to claim 2 or 3, wherein said acid is a member selected from the group consisting of $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$, $\text{HO}_3\text{S}(\text{CF}_2)_n\text{SO}_3\text{H}$ where n is an integer having a value of 0 to 9, sulfuric acid, HCl, HBr, phosphoric acid and HNO_3 , and any mixtures thereof.
- 10 14. A matrix according to claim 13, wherein said acid is selected from $\text{CF}_3(\text{CF}_2)_n\text{SO}_3\text{H}$ or $\text{HO}_3\text{S}(\text{CF}_2)_n\text{SO}_3\text{H}$, wherein n is equal to 0,1,2,3 or 4.
15. A matrix according to claim 14, wherein said acid is used in an aqueous solution having a molar concentration of 10 to 99%.
16. A matrix according to claim 15, wherein said acid is used in an
15 aqueous solution having a molar concentration of 25 to 99%.
17. A membrane comprising the ion conducting matrix of any one of the preceding claims, wherein said inorganic material is electronically non-conductive material.
18. A membrane according to claim 17, wherein the inorganic powder of
20 the matrix comprises particles that are essentially of a size of less than 150 nm.
19. A membrane according to claim 17, wherein said membrane comprises pores with a size which is essentially smaller than 50 nm.
20. A membrane according to any one of the claims 17 to 19, wherein the
25 inorganic powder of the matrix is treated with an acid or a base prior to the preparation of the membrane.
21. A membrane according to any one of claims 17 to 20 which further comprises an electronic non-conductive reinforcing element.

22. A composite electrode comprising 10 to 70% by volume of the matrix of any one of claims 1 to 16 and the balance is an electrode material.

23. A method for casting a membrane of claims 17 to 21 which comprises the following steps:

5 (i) preparing a mixture comprising an inorganic powder, a polymeric binder that is chemically compatible with an aqueous electrolyte, at least one solvent characterized in having a high boiling point of above 100⁰C and at least one low boiling point solvent, having a boiling point lower than
10 that of the high boiling point solvent(s), in which the polymeric binder is soluble or form a gel at the casting temperature;

(ii) casting a film out of the mixture;

15 (iii) allowing the low boiling point solvent to evaporate from the mixture, thus forming a solid film;

(iv) washing the solid film and replacing the high boiling point solvent with the aqueous electrolyte solution to be included in the membrane.

20 24. A method for casting a composite electrode of claim 22 which comprises the following steps:

(i) preparing a mixture comprising an inorganic powder, a polymeric binder that is chemically compatible with an aqueous electrolyte, at least one solvent characterized in having a high boiling point of above 100⁰C, at least one low

boiling point solvent, having a boiling point lower than that of the high boiling point solvent(s) in which the polymeric binder is soluble or form a gel at the casting temperature, and a further powder comprising electrode material;

- 5 (ii) casting a film out of the mixture;
- (iii) allowing the low boiling point solvent to evaporate from the mixture, thus forming a solid film;
- (iv) washing the solid film and replacing the high boiling point solvent with the aqueous electrolyte solution to be included in the membrane.
- 10

25. A method according to claim 23 or 24, wherein the high boiling solvent is a water soluble solvent.

26. A method according to claim 23 or 24, wherein the high boiling point solvent is selected from the group consisting of propylene carbonate, ethylene carbonate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate and the like or any combinations thereof.

15

27. A method according to claim 23 or 24, wherein the low boiling point solvent is a member selected from the group consisting of tetrahydrofuran, DME, cyclopentanone, acetone, N-methyl pyrrolidone, dimethylacetamide, methylethylketone, dimethyl-formamide, or any combination thereof.

20

28. A method for preparing a membrane of claims 17 to 21 by extrusion which comprises the following steps:

- (i) preparing a mixture comprising an inorganic powder, a polymeric binder that is chemically compatible with an aqueous electrolyte and at least one solvent characterized in having a boiling point of above 90°C in which the polymeric binder is at least partially soluble or form a gel at extrusion temperature;
- 25

- (ii) heating the mixture to its softening temperature;
- (iii) forming a film out of the mixture by hot extruding the softened mixture;
- (iv) cooling the film thus formed;
- 5 (v) washing the solid film and replacing the solvent with the aqueous electrolyte solution to be included in the membrane.

29. A method for preparing a composite electrode of claim 22 by extrusion which comprises the following steps:

- 10 (i) preparing a mixture comprising an inorganic powder, a polymeric binder that is chemically compatible with an aqueous electrolyte, at least one solvent characterized in having a boiling point of above 90°C in which the polymeric binder is at least partially soluble or forma gel at extrusion temperature and a further powder comprising electrode material;
- 15 (ii) heating the mixture to its softening temperature;
- (iii) forming a film out of the mixture by hot extruding the softened mixture;
- (iv) cooling the film thus formed;
- 20 (v) washing the solid film and replacing the solvent with the aqueous electrolyte solution to be included in the membrane.

30. A method according to claim 28 or 29, wherein said solvent is a water soluble solvent.

31. A method according to claim 28 or 29, wherein said solvent is a
25 member selected from the group consisting of propylene carbonate, diethyl carbonate, dimethyl carbonate, butyrolactone, methyl isoamyl ketone, cyclohexanone, dialkyl phthalate, glycerol triacetate or any combinations thereof.

32. An electrochemical cell comprising a membrane of any one of claims 17 to 21.
33. An electrochemical cell comprising at least one electrode of claim 22.
- 5 34. An electrochemical cell according to claim 32 or 33, wherein said electrode material is a member selected from the group consisting of carbon, graphite and a combination thereof.
35. An electrochemical cell according to claim 32 or 33, wherein the anode active material is selected from Cd, Zn, Al or their alloys and the
10 cathode active material is selected from MnO_2 , silver oxides and NiOOH .
36. An electrochemical cell comprising a membrane as defined in any one of claims 17 to 21, a Zn or Al anode and oxygen or air electrode which consists of a double layer film, wherein the air side is hydrophobic and the side close to the ionic membrane is hydrophilic.
- 15 37. An electrochemical cell according to claim 36, wherein the air electrode catalysts are compatible with the aqueous solution of the ionic conductive membrane and are selected from Pt, Pd, Au, Ag, Cu, Mn, W the oxides thereof or metal-porphyrin complexes of these salts.
38. An electrochemical cell according to claim 32 or 33, wherein said
20 electrode material is a metal oxide selected from among RuO_2 , WO_x , and MnO_2 .
39. An electrochemical cell according to claim 32 or 33, wherein said cell is a single structure unit manufactured by hot pressing the electrodes on both sides of a membrane of claims 17 to 21.
- 25 40. A fuel cell comprising an ion conducting membrane of any one of claims 17 to 21.
41. A water electrolyzer comprising an ion conducting membrane of any one of claims 17 to 21.

Figure 1.

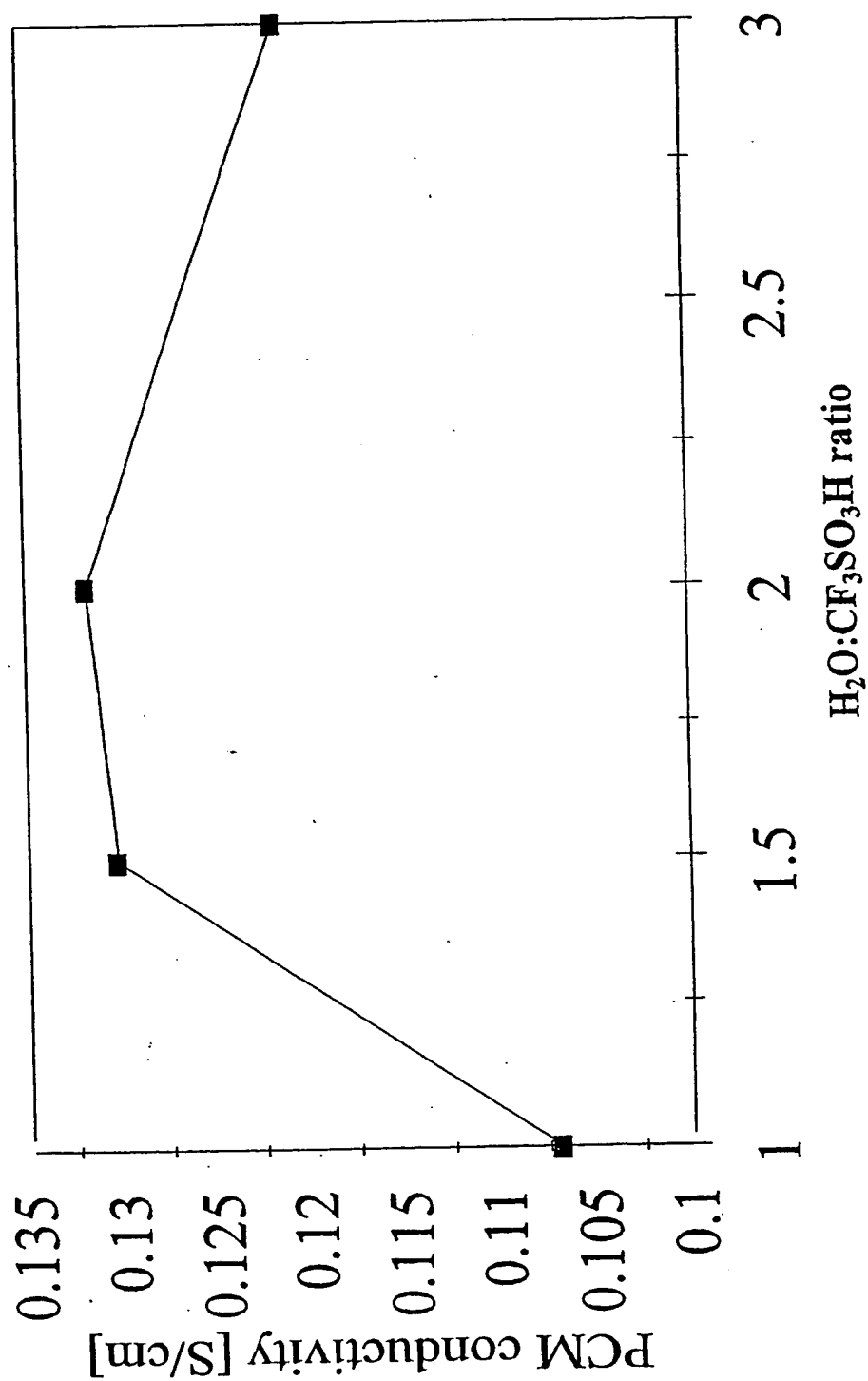
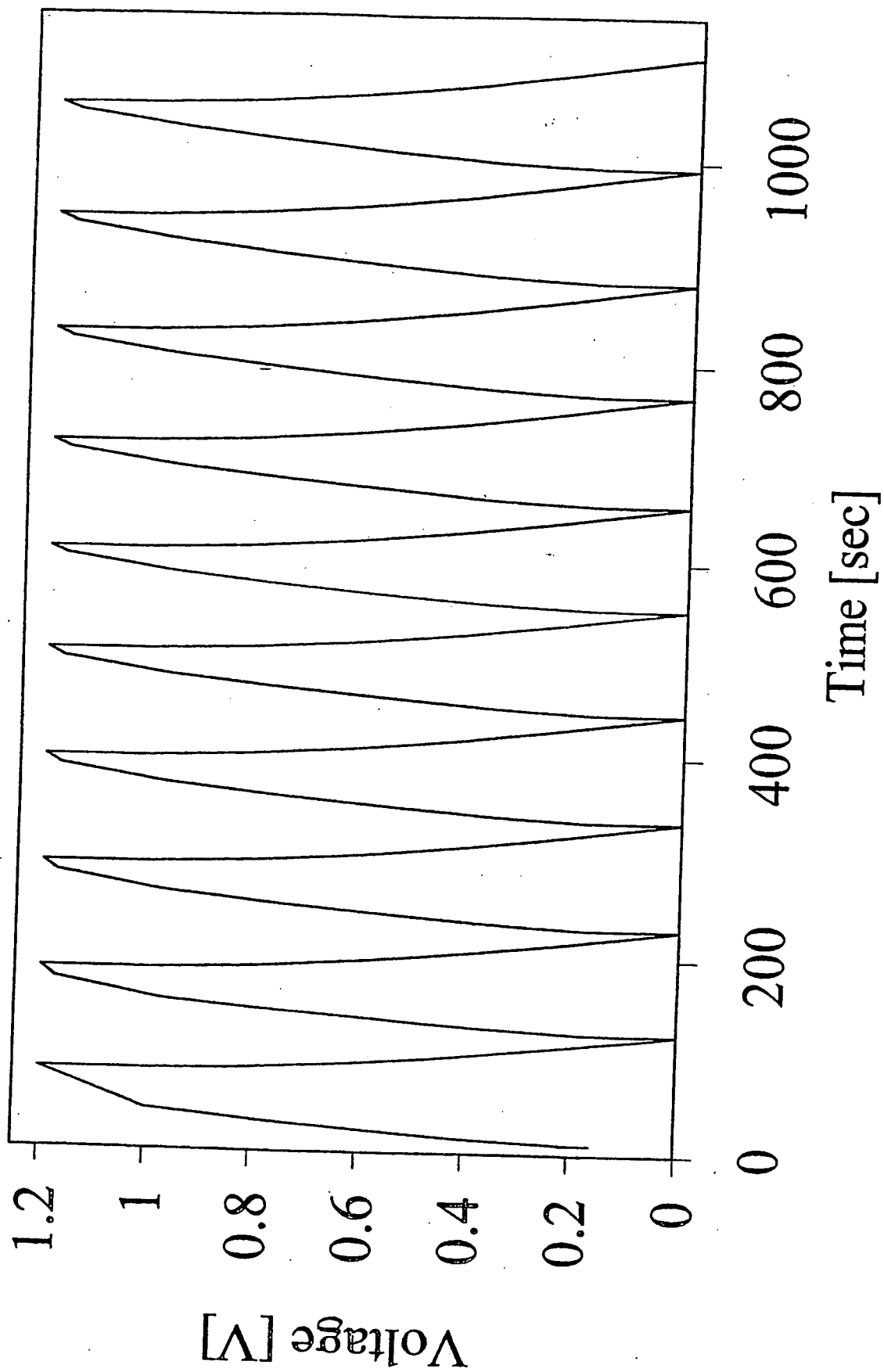


Figure 2.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL99/00109

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,780,954 A (KATO) 01 November 1988, see abstract; col. 2, line 19 - col. 3, line 11; col. 4, lines 23-68 and Example 1-4.	1- 41
Y	US 4,687,715 A (MICHAEL) 18 August 1987, see abstract; col. 2, lines 6-65; col. 3, line 5 - col. 4, line 34; col. 5, lines 21-51.	1-5, 7, 8, 17, 20-22, 32-34, 39, 40
Y	US 4,895,775 A (KATO et al) 23 January 1990, see abstract; col. 2, line 20 - col. 3, line 9; col. 4, lines 47-68; col. 5, lines 18-21 and 50-53.	1-8, 12, 13, 15-17, 20-22, 32-34, 39, 40
Y	US 5,709,786 A (FRIESE et al) 20 January 1998, see abstract; col. 2, lines 1-12 and 33-61; col. 3, lines 34-39; col. 4, lines 20- 40.	1-41



Further documents are listed in the continuation of Box C.



See patent family annex.

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A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

05 MAY 1999

Date of mailing of the international search report

25 MAY 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL99/00109

A. CLASSIFICATION OF SUBJECT MATTER: IPC (6):

H01M 4/58, 6/14, 6/18, 6/16, 4/86, 4/62, 4/34, 4/32, 4/50, 4/42, 6/00; C25B 11/04, 13/00, 9/00; C08J 5/20; B23P 19/00

A. CLASSIFICATION OF SUBJECT MATTER: US CL :

429/40, 41, 42, 44, 217, 218.1, 219, 222, 223, 224, 229, 231.8, 300, 303, 324, 326, 330, 331, 338, 342; 204/296, 291, 252; 521/27; 29/623.1, 623.5, 745, 746

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

429/40, 41, 42, 44, 217, 218.1, 219, 222, 223, 224, 229, 231.8, 300, 303, 324, 326, 330, 331, 338, 342; 204/296, 291, 252; 521/27; 29/623.1, 623.5, 745, 746

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